

NOVEL BIODEGRADABLE ESTER-BASED POLYMER BLENDS

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ABSTRACT We have found, within the polyester family, interesting and potentially useful patterns of three-component compatibility. The bacterially produced biodegradable polyester, poly(hydroxybutyrate) (PHB) and its copolymers with hydroxyvalerate (HV) together with polymers such as cellulose acetate butyrate (CAB), polycaprolactone, poly(lactic acid), and a series of high-molecular-weight, non-crystallizable ester-based plasticisers have been identified as possible candidates in the production of blends in which aspects of performance can be varied with a degree of independence of cost. The compatibility ranges can be conveniently represented in the form of triangular graphs, with the relative weight fraction, or percentage, being represented along each of the three axes. The extent to which the modulation of the physical properties in general, but the stability in various environments in particular, is possible by the formation of three-component blends, such as those formed between P(HB-HV), cellulose acetate butyrate and poly(alkylene adipate) plasticisers, is discussed.

INTRODUCTION

Microbially produced polyesters, such as poly(3-hydroxybutyrate), have unique structures and characteristics. One of the problems associated with these materials is that the precision of the biological synthesis is not readily adapted to produce structural variations. Similarly, although there exists an established range of hydrolytically or biologically degradable polyesters, their commercial availability often reflects relative ease of synthesis, rather than deliberate design of structure to produce a particular balance of properties.

Whilst it is well established that the properties of a particular polymer can be extended by blending with other polymers, compatibility restrictions frequently limit the versatility of this approach. For this reason, three-component blends are rarely a practical solution to the problem of modulating and extending the performance and price of particular groups of polymers. Following our earlier work on blends of polycaprolactone with hydroxybutyrate-hydroxyvalerate copolymers⁽¹⁾ we have found that within the polyester family, interesting and potentially useful patterns of three-component compatibility can be established. This paper describes the extent to which the modulation of the physical properties in general, but the stability in various environments in particular, is possible by the formation of three-component blends of these polymers. Investigations have been restricted to those molecular

weight ranges of hydroxybutyrate polymers that produce acceptable mechanical properties in the unblended materials ($M_w > 300\,000$).

EXPERIMENTAL

Materials

PHB and P(HB-HV) copolymers

| % HV content | M_w | Supplier |
|--------------|----------|---------------------------|
| 0 (BIOMER) | $> 10^6$ | Biomer, Kralling, Germany |
| 0 | 786 000 | ICI (Zeneca), Teeside, UK |
| 5 | 350 000 | ICI (Zeneca), Teeside, UK |
| 8 | 350 000 | ICI (Zeneca), Teeside, UK |
| 12 | 335 000 | ICI (Zeneca), Teeside, UK |
| 20 | 397 000 | ICI (Zeneca), Teeside, UK |

Poly(DL-lactide) 650 000 (M_v) Purac Biochem bv, Gorinchem, Holland

Polycaprolactone

Tone 767 80 000 (M_w) Union Carbide, Rickmansworth, Herts.

Cellulose acetate butyrate Eastman Chemical (UK) Ltd, Hemel Hempstead

| Code: | % acetyl | % butyl | % hydroxyl | Molecular weight (M_n) |
|------------|----------|---------|------------|----------------------------|
| CAB 531-1 | 3.0 | 50 | 1.7 | 40 000 |
| CAB 381-2 | 13.5 | 38 | 1.3 | 40 000 |
| CAB 381-20 | 13.5 | 37 | 1.8 | 70 000 |

Polymeric plasticizers

| | M_w | M_n |
|--|--------|-------|
| Polyester glutarate Plastahall P-7092 | 8 400 | 3 500 |
| Polyester adipate Paraplex G40 | 23 500 | 5 900 |
| Polyester adipate, Plastahall P-650 | 5 300 | 2 700 |
| Epoxidised soya bean oil, Paraplex G62 | 2 000 | 1700 |

Used as supplied by Croxton & Garry Ltd, Dorking, UK (distributors for C P Hall & Co, Chicago, USA).

Preparation of samples

Following initial experiments, a standard protocol was established for solvent and melt blending. In the case of solvent blending, 10% (w/v) solutions of the individual components (P(HB-HV) copolymers, CAB, polymeric plasticisers) were prepared in chloroform. The required compositions of the three-component blends were obtained by mixing the solutions and pouring onto glass Petri dishes. The solvent was allowed to evaporate slowly over a

period of several days before the films were removed and annealed at 90°C for 24 hours. Films were stored at 20°C before testing. Melt blending of the individual multi-component compositions was carried out at 160-170°C on a two-roll laboratory mill and films were subsequently pressed at 165-180°C using an electrically heated (Daniels, UK) press.

Comment on grades used and variations observed

The grades of cellulose acetate-butyrate used had differing degrees of substitution, although the contribution from this to the compatibility of the blends containing these was minimal. The effects of the structural changes of the cellulose esters used in our studies were slightly more pronounced in the temperature requirement for melt processing and also in the contribution to the mechanical properties of the blends.

RESULTS AND DISCUSSION

Solvent-mediated and melt processing of PHB

In a series of initial experiments, the bacterially produced biodegradable polyester, poly(hydroxybutyrate) (PHB), and its copolymers with hydroxyvalerate (HV) together with polymers such as cellulose acetate butyrate (CAB), polycaprolactone (PCL), poly(lactic acid) (PLA), and a series of high-molecular-weight, non-crystallizable ester-based plasticisers were examined using solvent blending techniques. It was observed that three distinct types of blend were obtained, which were readily characterised as optically clear, opaque, or translucent.

A systematic examination was then undertaken of the range of two- and three-component blends of P(HB-HV) copolymers with cellulose acetate butyrate (CAB) and a series of commercially available polymeric plasticisers (polyester glutarate: Mn 8400, code P92; polyester adipate: Mn 15 000, code G40; and epoxidized soya bean oil: Mn 2000, code G62). Films of the various combinations were prepared by solvent evaporation from chloroform. Three distinct areas of apparent compatibility were observed. Blends containing high levels of CAB and low levels of plasticiser were found to be optically clear, whilst many of those containing high levels of plasticiser were found to be completely opaque. A substantial number of the blends prepared, particularly those with intermediate levels of plasticiser, were translucent. The most convenient way of representing these variations was found to be with a three-coordinate, or triangular, graph. Figure 1 shows a typical three-coordinate phase diagram, that obtained with 12% HV P(HB-HV) copolymer,

CAB and polyester glutarate. The general shape of the graphs obtained with the other two plasticisers was very similar as were those produced from blends prepared by conventional melt blending techniques using a two-roll mill, followed by melt pressing into film form. In all these cases the three distinct types of blend (clear, translucent and opaque) occurred in the same regions on the graph. The only variations observed between them can be summarised as relatively modest changes in the positions of the transition from clear to translucent, especially on the plasticiser axis of the graph. It is well established that blend compatibility is affected by variables associated with the preparation related to the polymer, such as molecular weight and molecular weight distribution. Within the range of such variables that it was possible and relevant to study here, the overall variations in the appearance of the three-coordinate phase diagrams based on the P(HB-HV) copolymers was limited.

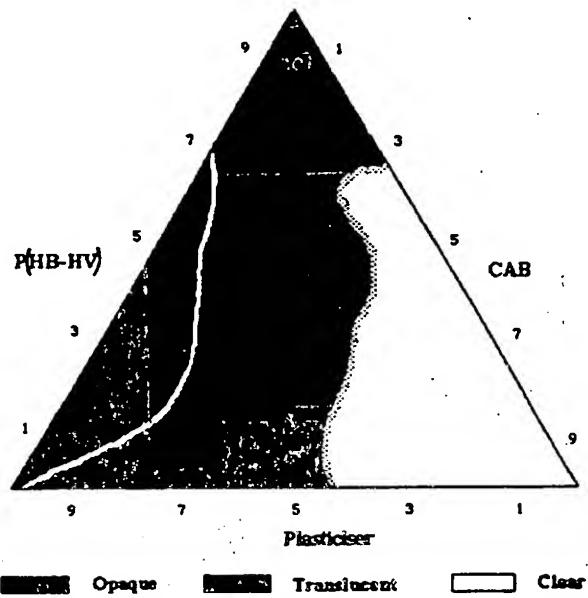


Figure 1 Three-coordinate phase diagram for 12% HV P(HB-HV)/CAB/polyester glutarate

Measurement of the glass transition temperature (T_g) by differential scanning calorimetry (DSC) was used to investigate the compatibility of the range of the blends. Polymers in the opaque region of the phase diagrams were found to exhibit multiple glass transitions, consistent with the incompatibility that was apparent from the optical properties of the blends. Similarly, the optically clear regions of the phase diagrams produced thermograms with single broad glass transitions that were consistent with the compatibility inferred from

their optical clarity. The translucent regions were more difficult to study. They were generally associated with substantial crystallinity and it was difficult to obtain unambiguous evidence of multiple glass transitions. The overall conclusion was that there was no uniform and substantial incompatibility associated with the translucent regions of the phase diagrams but that these blends did not show the single unique types of compatibility behaviour found in the clear and opaque regions.

The mechanical properties of these blends were investigated by preparing standard test pieces from the 100-200- μ thick sheets prepared by solvent and melt blending. The mechanical properties of the base P(HB-HV) copolymer were found to be affected in a fairly regular manner by the level of CAB and plasticiser incorporated: Blends high in CAB were found to have higher strength and lower flexibility than those containing high levels of plasticiser. Typical results for tensile strength and elongation at break are shown in Figures 2 and 3, respectively, which are for solvent-cast films of 12% HV P(HB-HV)/CAB/polyester glutarate blends.

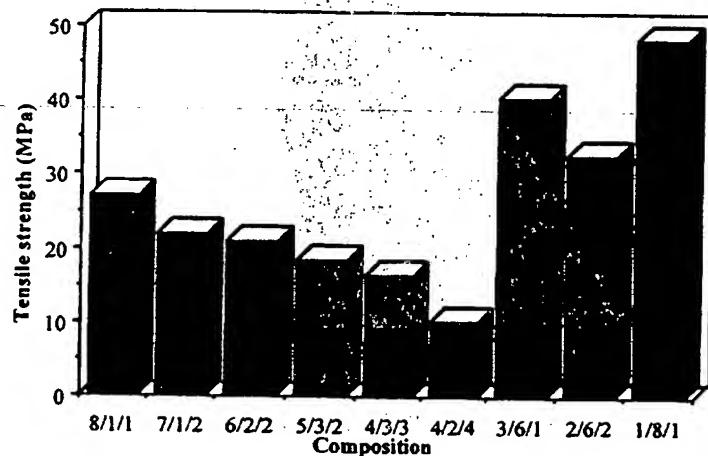


Figure 2 Tensile strength of solvent-cast 12% HV P(HB-HV)/CAB/polyester glutarate

The variation of physical properties of the blends with method of preparation was studied. Melt blending was found to increase the tensile strength of the films and for blends containing higher levels of CAB, somewhat improved flexibility. This is probably due to the more efficient mixing of the components by melt blending, enabling greater plasticization of the stiff CAB molecules by the plasticiser. Similarly, the increase in the tensile strength from solvent-cast to melt-blended specimens could well be due to the

amount of crystallinity induced by the different processing technique. Melt processing increases the crystallinity of the sample as evident from Figures 4 and 5, which illustrate the x-ray diffraction traces of solvent-cast and melt-pressed films for the P(HB-HV)/CAB/polyester adipate 8/1/1 and 1/8/1 blends, respectively.

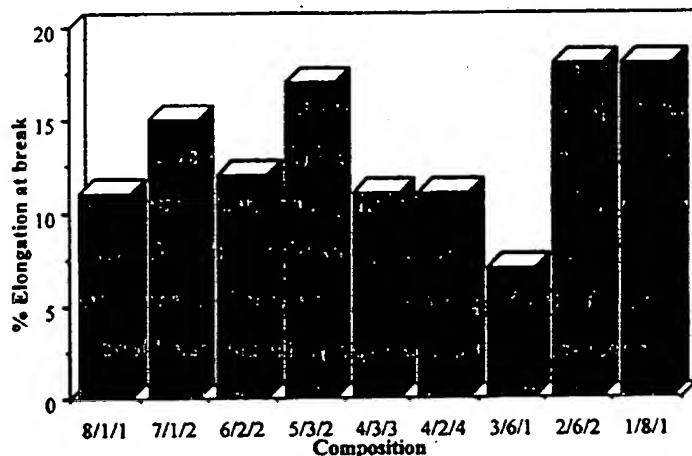


Figure 3 Elongation at break of solvent-cast 12% HV P(HB-HV)/CAB/polyester glutarate blends

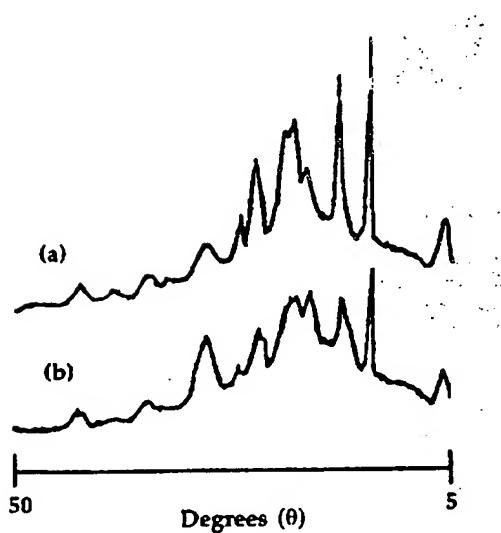


Figure 4
X-ray diffraction traces of P(HB-HV) (12%
HV)/CAB/polyester adipate 8/1/1 blend
(a) melt-pressed films, (b) solvent-cast films

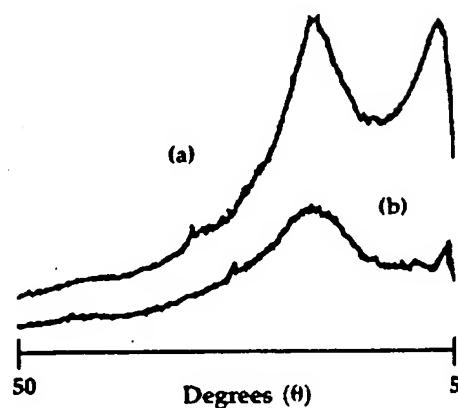


Figure 5
X-ray diffraction traces of P(HB-HV) (12%
HV)/CAB/polyester adipate 1/8/1 blend
(a) melt-pressed films, (b) solvent-cast films

Solvent-mediated and melt blending

A range of two- and three-component blends of PCL with cellulose acetate butyrate (CAB) and polymeric plasticisers (polyester glutarate (P92), polyester adipate (G40 and P650), and epoxidised soya bean oil (G62)), were prepared to enable construction of three-coordinate phase diagrams, based on optical clarity. The three-coordinate phase diagram for PCL/CAB/polyester glutarate is shown in Figure 6; phase diagrams for the polyester adipate and soya bean oil plasticisers look very similar. The mechanical properties of these blends again show interesting trends; as with the P(HB-HV) systems with increasing plasticiser, there is generally an increase in flexibility and greater strength with increasing cellulose acetate butyrate content. The physical properties of the PCL/CAB/plasticiser blends were also found to be affected by processing. The tensile strength and elongation at break for solvent-cast and melt-pressed PCL/CAB/polyester glutarate blends is shown in Table 1. Melt blending produced significantly higher levels of crystallinity and some movement in the position of the transition between opaque and translucent region of the phase diagram.

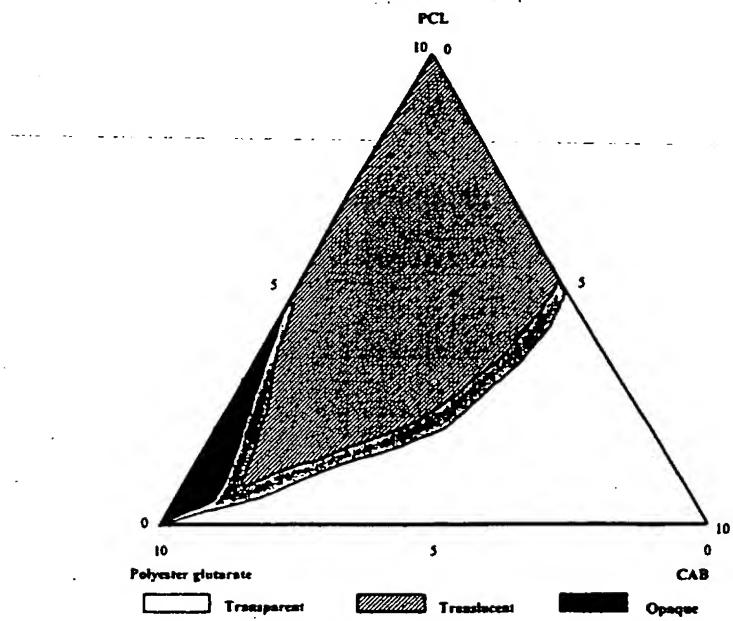


Figure 6 Three-coordinate phase diagram for PCL/cellulose acetate butyrate/polyester glutarate blends

Hydrolytic degradation studies

The hydrolytic degradation rates of a number of two- and three-component blends, including the individual components of the blend was studied at high temperature and pH. The use of

both high pH and temperature to accelerate the degradation of P(HB-HV) copolymers is well documented⁽²⁻⁴⁾. This enables hydrolytic rates to be obtained in shorter time period. The rates of degradation can be obtained by comparing the time period required for 10% (t_{10}) and 50% (t_{50}) dry weight loss. This information is presented in Tables 2-4, below for a number of blends.

Table 1 Effect of processing on tensile strength and elongation at break of PCL/CAB/polyester glutarate blends

| PCL/CAB/P92 blend composition | Melt-pressed film | | Solvent-cast film | |
|-------------------------------------|------------------------------|-------------------------------|------------------------------|-------------------------------|
| | Tensile strength (MPa) | Elongation at break (%) | Tensile strength (MPa) | Elongation at break (%) |
| 10/0/0 | 22.8 | 731 | 19.1 | 190 |
| 8/1/1 | 20.6 | 891 | 13.5 | 379 |
| 6/3/1 | 17.2 | 486 | 15.7 | 328 |
| 3/6/1 | 11.2 | 87 | 20.4 | 104 |
| 1/8/1 | 16.6 | 33 | 25.8 | 20 |
| 0/10/0 | 25.2 | 33 | 38 | 22 |

Table 2 The times for 10% (t_{10}) and 50% (t_{50}) weight loss of P(HB-HV) copolymers, CAB and blends in pH 10.6 buffer at 70°C

| Blend | t_{10} (days) | t_{50} (days) |
|---------------------------|-----------------|-----------------|
| P(HB-HV) (12% HV) | 3.9 | 13.5 |
| P(HB-HV) (20% HV) | 2.8 | 6.0 |
| CAB | 46 | - |
| P(HB-HV) (12% HV)/CAB 9/1 | 8.1 | 15.6 |
| P(HB-HV) (12% HV)/CAB 1/9 | 25 | - |

Table 3 The times for 10% and 50% weight loss of PHB and P(HB-PHV) (12% HV) copolymers and blends with epoxidised soya bean oil in pH 10.6 buffer at 70°C

| Blend | t_{10} (days) | t_{50} (days) |
|---------------------------|-----------------|-----------------|
| PHB/G62 9/1 | 9.1 | 41.1 |
| PHB/G62 8/2 | 6.9 | 36 |
| PHB/G62 7/3 | 4.1 | 27.8 |
| PHB/G62 6/4 | 3 | 18 |
| PHB/G62 5/5 | 1.7 | 6 |
| P(HB-HV) (12% HV)/G62 9/1 | 3.0 | 12.4 |
| P(HB-HV) (12% HV)/G62 8/2 | 1.6 | 4.4 |
| P(HB-HV) (12% HV)/G62 7/3 | 1.1 | 3.5 |
| P(HB-HV) (12% HV)/G62 6/4 | 0.8 | 3 |
| P(HB-HV) (12% HV)/G62 5/5 | 0.3 | 1.3 |

Table 4 The times for 10% and 50% weight loss of P(HB-HV) (12% HV) copolymers and blends with CAB and epoxidised soya bean oil in pH 10.6 buffer at 70°C

| Blend | t_{10} (days) | t_{50} (days) |
|---------------------------------|-----------------|-----------------|
| P(HB-HV) (12% HV)/CAB/G62 7/1/2 | 2.0 | 6.2 |
| P(HB-HV) (12% HV)/CAB/G62 6/2/2 | 2.5 | 8.4 |
| P(HB-HV) (12% HV)/CAB/G62 5/3/2 | 3.2 | 11.8 |
| P(HB-HV) (12% HV)/CAB/G62 4/3/3 | 2.9 | 7.4 |
| P(HB-HV) (12% HV)/CAB/G62 4/2/4 | 1.5 | 4.6 |

The level of both CAB and the plasticiser influence the hydrolytic stability of the blends. Increasing the levels of CAB was found to cause the blends to be more resistant to hydrolytic degradation, but with increasing the level of plasticiser, the blends degraded faster, for both two- and three-component blends. These effects were systematic and predictable for the three-component blends on the basis of the rates of degradation of the individual components.

Although the use of high temperature and pH enables hydrolytic rates to be obtained in shorter time periods, and is useful in predicting relative degradation behaviour at ambient conditions, it does not enable the prediction of absolute rates. It is important, therefore, to collect data at ambient temperature and close to physiological pH, in order that the contribution of simple hydrolysis in subsequent microbiological degradation experiments may be estimated. For this reason the hydrolytic degradation rates of a number of two- and three-component blends, including the individual components of the blend was studied at 25°C in pH 7.4 buffer.

Studies of the percentage change in the initial dry weight for the P(HB-HV) (20% HV) copolymer, CAB and the P(HB-HV) (20% HV)/CAB 9/1 and P(HB-HV) (20% HV)/CAB 1/9 blends were carried out in pH 7.4 phosphate buffer at 25°C. The degradation profiles of all the samples are characterized by an initial slow weight loss, followed by a secondary enhanced phase. The rate of all the samples, as expected, is much slower under these milder conditions compared with those used in the accelerated degradation (pH 10.6 and 70°C). Whereas the P(HB-HV) (12% HV) copolymer had a t_{10} (time for 10% loss in initial dry weight) of 3.9 days in pH 10.6 and 70°C, in pH 7.4 at 25°C, after 174 days the weight loss is less than 8%. The incorporation of 10% P(HB-HV) into the CAB matrix has the

effect of slightly increasing the degradation rate of the blend in comparison to the unblended CAB.

Addition of the polymeric plasticiser (polyester glutarate, P92) into the P(HB-HV) copolymer matrix had the effect of increasing the degradation rate of the blend in comparison to the unblended copolymer. The effect of increasing the plasticiser from 10 to 30% is quite marked in the early stages of degradation. In the ternary blends of P(HB-HV)/CAB/P92, with high contents of CAB, the blend is more resistant to hydrolytic degradation. The contribution of the plasticiser in increasing the degradation rate is only evident with blends high in P(HB-HV) copolymer content. Processing also was found to have an effect on the hydrolytic degradation rate. Solvent-mediated blends were found to lose weight faster than those prepared using melt-blending techniques, probably due to the higher crystallinity of samples prepared from melt-blending techniques.

Results from the hydrolytic degradation of PCL and its blends with CAB and polymeric plasticisers at 25°C and pH 7.4 were found to show similar trends with those of the P(HB-HV)/CAB/plasticiser blends. There is marked difference in the profiles for the melt-pressed and solvent-cast films, probably due again to differences in the crystallinity of the samples.

Abiotic (hydrolytic) degradation and biodegradation in different environments

The aerobic degradation of PHB, CAB, polymeric plasticisers and P(HB-HV)/CAB/plasticiser blends using 10% activated sludge (mixed inoculum) at 25°C by Dr Wolf Muller and his colleagues at the Water Resources Institute, Stuttgart University showed very interesting results, which will be published in detail in subsequent joint publications. Two points are worth comment here.

The use of oxygen consumption as a monitoring technique very effectively shows the complete biodegradation of PHB and P(HB-HV) copolymers to occur within a month. For the first three days or so, however, there is an effective lag time, with no effective biodegradation occurring. We have previously shown the value, in degradation studies, of goniophotometry, a technique which involves the measurement of the intensity of light reflected from a surface, as a function of viewing angle^(5,6). The scattering envelope produced is governed by the rugosity or roughness of the surface and hence this technique is

useful in following changes in rugosity resulting from erosional processes which affect the surface. Three important parameters may be derived from the goniophotometric curve. These are: the intensity of light scattered at the specular angle (I_s), the diffuse reflectance (I_d) and the peak width at half-height ($W_{1/2}$). These three quantities, (I_s , I_d and $W_{1/2}$), are combined together to give a very useful single parameter, the so-called 'gloss factor' (GF). Use of this technique in the study of the early stages of degradation in the activated sludge model showed unambiguously (Table 5) that surface degradation proceeds actively during the apparent lag time.

Table 5 Goniophotometric parameters curves for 20% HV P(HB-HV) copolymer in the early stages of degradation in the Stuttgart University activated sludge system

| Degradation time (h) | I_s | I_d | $W_{1/2}$ (degrees) | Gloss Factor |
|----------------------|-------|-------|---------------------|--------------|
| 0 | 1780 | 70 | 3.0 | 570 |
| 7 | 1400 | 75 | 3.0 | 441 |
| 15 | 1100 | 82 | 2.9 | 351 |
| 24 | 940 | 95 | 4.3 | 196 |
| 72 | 140 | 110 | 18.0 | 1.7 |

The second point of significance relating to the degradation studies in activated sludge relates to the behaviour of CAB. Whereas the P(HB-HV)-copolymers and all the polymeric plasticiser blends used in this study were found to be biodegradable, CAB proved to be resistant to degradation. Unlike the hydrolysis studies where its contribution was proportional to level of incorporation, in the activated sludge degradation studies, even 10% of CAB had a disproportionate inhibitory effect. After examining possible explanations for this behaviour, we have come to the conclusion that its compatibility with the amorphous regions of P(HB-HV) stabilises them to biodegradation in the system used here. This effect does allow hydrolytic (abiotic) and biodegradation to be independently manipulated to some extent by composition variation.

It is clear that the rate of biodegradation is very dependent upon the biological environment in which the polymer is exposed and that as yet no rationale has been developed to link polymer structure with its susceptibility to different microbiological species. We have a range of ongoing studies both within the laboratory and in various external environments to extend our knowledge base in this area. An example of this has been the comparative effects at various soil exposure sites around the world in comparison to a standard laboratory compost. The most aggressive soil site that we have encountered is in Mirpur, Jammu

Kashmir. Films of 12% HV P(HB-HV) copolymer (weight-average molecular weight 397 000) were exposed in Mirpur and in a standard compost model at 25°C. After a thirty-day period the samples in compost had lost 10% of their initial dry weight, whereas those exposed in soil at Mirpur had lost 25% of their initial dry weight.

It is well established that blend compatibility is affected by variables associated with the preparation technique, such as solvent temperature and processing parameters, and those related to the polymer, such as molecular weight and molecular weight distribution. Within the range of such variables that it was possible and relevant to study here, the overall variations in the appearance of the three-coordinate phase diagrams based on the P(HB-HV) copolymers were limited. Maximum sensitivity to copolymer composition, molecular weight and preparation method was found down the left-hand side of phase diagrams such as those shown in Figures 1 and 6. This is the region of maximum incompatibility and minimum utility of the blends. Maximum stability and minimum variability is found towards the right-hand side of the diagrams where the most compatible and most useful blends are located.

As a result it has been found possible to produce potentially useful blends in which aspects of performance can be varied independently of cost. The compatibility ranges are conveniently represented in the form of triangular graphs, our subsequent work has involved the use of these blends as carriers for fabrication of test pieces to enable the study of microbiological attack on novel polymers, available in only limited quantity. This has been part of a programme designed to identify polymer systems that possess specific susceptibility to microbiological attack which will then promote degradation of the host polymer matrix.

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REFERENCES

1. Polymers for biodegradable medical devices (X) - Hydroxybutyrate-hydroxyvalerate copolymers: physical and degradative properties of blends with polycaprolactone. M Yasin and B J Tighe. *Biomaterials*, 13 (1992) 9-16.

- 2: Polymers for biodegradable medical devices (II) - Hydroxybutyrate-hydroxyvalerate copolymers: hydrolytic degradation studies. S J Holland, A M Jolly, M Yasin and B J Tighe. *Biomaterials*, 8 (1987) 289- 295.
3. Polymers for biodegradable medical devices (VI) - Hydroxybutyrate-hydroxyvalerate copolymers: accelerated degradation of blends with polysaccharides. M Yasin, S J Holland, A M Jolly and B J Tighe. *Biomaterials*, 10 (1989) 400-412.
4. Strategies for the design of biodegradable polymer systems: manipulation of polyhydroxybutyrate-based blends. M Yasin and B J Tighe. *Plast. Rubber Compos. Process. Appl.*, 19 (1993) 15-27.
5. New biodegradable three component polymer blends. M Yasin, A J Amass, B J Tighe, P Püchner and W R Müller. *The 1994 IChemE Research Event, Abstracts 1* (1994) 368-370.
6. Biodegradable polymer blends. M Yasin, A J Amass, B J Tighe. *Polymers and Other Advanced Materials*, editors P N Prasad, J E Mark and J F Tung. Plenum Publishing, New York 1996, 169-176.

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